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United States Department of Agriculture,

BUREAU OF CHEMISTRY—Circular No. 29.

H. W. WILEY, Chief of Bureau.

CHANGES IN PROVISIONAL METHODS FOR THE ANALYSIS OF FOODS AND ADDITIONS THERETO, FROM 1902 TO 1905.[a]

INTRODUCTION.

The methods for the examination of foods, with special reference to the detection of adulteration, submitted at the meeting of the Association of Official Agricultural Chemists in 1901, were adopted provisionally and printed as Bulletin 65 of the Bureau of Chemistry. When these methods were adopted it was expected that they would be greatly amplified and changed as a result of subsequent study. Many of the methods appearing in Bulletin 65 had been carefully worked out by the association, but only a few of them were tested by collaborative work, and in many cases the methods that seemed to be best adapted for making certain determinations were adopted provisionally without detailed investigation by the association. It is seen, therefore, that the methods in Bulletin 65 were adopted as a working basis, and probably conditions would have been simplified if these methods had first been adopted as tentative rather than as provisional.

Since the publication of Bulletin 65 many methods have been adopted for subjects not covered in that report, and new methods and modifications have been made provisional. Upon attempting a revision of Bulletin 65 it was found that the changes necessary and the rearrangement needed to meet the growth of the work and prevent duplication in statement, in both Bulletins 46[b] and 65, were so extensive that a satisfactory revision was impracticable (following the precedents established by the association) without special authorization. For that reason it has been thought best to publish at this time merely the additions and changes that have been authorized by the association, and to suggest at the next convention a comprehensive plan for the revision of all of the methods.

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[a] U. S. Dept. Agr., Bureau of Chemistry, Bul. No. 65, adopted by the Association of Official Agricultural Chemists, November 14–16, 1901.

[b] Methods of Analysis, adopted by the Association of Official Agricultural Chemists, November 11, 12, 14, 1898.

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In view of this general revision of the methods, as now contemplated, all members of the association and others interested are urged to call attention to any inaccuracies or inconsistent statements which come to their notice. The 1906 meeting of the association will probably occur at an earlier date than usual and prompt action is necessary.

W. D. Bigelow,
Chief, Division of Foods.

Washington, D. C., *April 24, 1906.*

I. MEAT AND MEAT PRODUCTS.

(All page references are to Bulletin 65.)

Twentieth Convention, 1903, Bul. 81, Cir. 13.

The method for precipitation by bromin alone and by bromin in the filtrate from zinc sulphate was discontinued.

This action eliminates from the methods the following paragraphs in Bulletin 65: Page 11, (e) Determination of proteoses, peptones, and gelatin, (1) First method; page 18, (e) Determination of proteoses, peptones, and gelatin; and page 19, (g) Determination of peptones.

Twenty-first Convention, 1904, Bul. 90, Cir. 20.

The following methods were adopted as provisional:

Examination of Meat Extracts.

Ammonia.—By the magnesium oxid method, as described in Bulletin 46, page 21.

Acidity.—Titrate with standard alkali solution, using litmus paper as an indicator. The solution may advantageously be removed from the beaker and placed on the litmus paper by means of a capillary tube.

Phosphorus.—The organic matter should be destroyed by one of the methods given in Bulletin 46, page 12, and phosphoric acid determined by either the gravimetric or volumetric molybdate method described in Bulletin 46, pages 12 and 14.

Chlorin.—Determine chlorin by titration with sulphocyanid, according to Volhard. For ordinary purposes the solution of the ash may be employed. More exact results may be obtained by dissolving about 1 gram of the meat extract in 20 cc of a 5 per cent solution of sodium carbonate, evaporating to dryness, and thoroughly igniting. The residue is then extracted with hot water, filtered and washed, after which the filter and contents are returned to a platinum dish and ignited. The contents of the dish are then dissolved in nitric acid, added to the filtrate, and the chlorin content determined as indicated above.

II. EDIBLE OILS AND FATS.

Twentieth Convention, 1903, Bul. 81, Cir. 13.

Page 26, just preceding "5. Determination of Saponification Number, etc." (under "4. Determination of Iodin Absorption, etc.") insert the Hanus method as a provisional optional method. (See additions for 1905 for text of method then made official.)

Page 32, under "16. Halphen Reaction for Cotton-Seed Oil," third line, before the word "brine" insert the word "saturated," and for "fifteen minutes" substitute "an hour to two hours." The second sentence then reads as follows:

Mix equal volumes of this reagent and the oil under examination and heat in a bath of boiling saturated brine for an hour to two hours.

Page 33, under "18. Renard's Test for Peanut Oil as Modified by Tolman," substitute the following (the change made consists in taking 20 grams of fat for analysis instead of 5, and increasing proportionally the reagents used as well as providing for an additional washing):

18. Renard's Test for Peanut Oil[a] as Modified by Tolman.

Weigh 20 grams of oil into an Erlenmeyer flask. Saponify with alcoholic potash, neutralize exactly with dilute acetic acid, using phenolphthalein as indicator, and wash into a 500-cc flask containing a boiling mixture of 100 cc of water and 120 cc of a 20 per cent lead acetate solution. Boil for a minute, and then cool the precipitated soap by immersing the flask in water, occasionally giving it a whirling motion to cause the soap to stick to the sides of the flask. After the flask has cooled, the water and excess of lead can be poured off and the soap washed with cold water and with 90 per cent (by volume) alcohol. Now add 200 cc of ether, cork the flask, and allow to stand for some time until the soap is disintegrated, then heat on the water bath, using a reflux condenser, and boil for about 5 minutes.[b] In the oils most of the soap will be dissolved, while in lards, which contain so much stearin, part will be left undissolved. Cool the ether solution of soap down to from 15° to 17° C., and let stand until all the insoluble soaps have crystallized out—about twelve hours are required.

[a] Comp. rend., 1871, **73**: 1330; Benedikt and Lewkowitsch, Oils, Fats, and Waxes, p. 365.

[b] Process used by N. J. Lane in his modification of Muter's method, J. Am. Chem. Soc., 1893, 15: 110.

Filter and thoroughly wash the precipitate with ether. Save the filtrate for the determination of the iodin number of the liquid fatty acids by the Muter method. The soaps on the filter are washed back into the flask by means of a stream of hot water acidified with hydrochloric acid. Add an excess of dilute hydrochloric acid, partially fill the flask with hot water, and heat until fatty acids form a clear, oily layer. Fill the flask with hot water, allow the fatty acids to harden and separate from the precipitated lead chlorid; wash, drain, repeat washing with hot water, and dissolve the fatty acids in 100 cc of boiling 90 per cent (by volume) alcohol. Cool down to 15° C., shaking thoroughly to aid crystallization. From 5 to 10 per cent of peanut oil can be detected by this method, as it effects a complete separation of the soluble acids from the insoluble, which interfere with the crystallization of the arachidic acid. Filter, wash the precipitate twice with 10 cc of 90 per cent (by volume) alcohol, and then with alcohol of 70 per cent (by volume). Dissolve off the filter with boiling absolute alcohol, evaporate to dryness in a weighed dish, dry and weigh. Add to this weight 0.0025 gram for each 10 cc of 90 per cent alcohol used in the crystallization and washing if done at 15° C.; if done at 20°, 0.0045 gram for each 10 cc. The melting point of arachidic acid obtained in this way is between 71° and 72° C. Twenty times the weight of arachidic acid will give the approximate amount of peanut oil present. No examination for adulterants in olive oil is complete without making the test for peanut oil.

The Hanus method (given in the Proceedings for 1903, Bul. 81, p. 63) was adopted as an official method for the determination of the iodin absorption of fats and oils.

HANUS METHOD.

(A) *Preparation of reagents.*

(1) *Iodin solution.*—(*a*) Dissolve 13.2 grams iodin in 1,000 cc glacial acetic 99.5 per cent acid (showing no reduction with bichromate and H_2SO_4): add enough bromin to double the halogen content determined by titration—3 cc of bromin is about the proper amount. The iodin may be dissolved by the aid of heat, but the solution should be cold when bromin is added.

(2) *Decinormal sodium thiosulphate solution.*—Dissolve 24.8 grams of chemically pure sodium thiosulphate, freshly pulverized as finely as possible and dried between filter or blotting paper and dilute with water to 1 liter at the temperature at which the titrations are to be made.

(3) *Starch paste.*—One gram of starch is boiled in 200 cc of distilled water for 10 minutes and cooled to room temperature.

(4) *Solution of potassium iodid.*—One hundred and fifty grams of potassium iodid are dissolved in water and made up to 1 liter.

(5) *Decinormal potassium bichromate.*—Dissolve 4.9066 grams of chemically pure potassium bichromate in distilled water, and make the volume up to 1 liter at the temperature at which the titrations are to be made. The bichromate solution should be checked against pure iron.

(B) *Determination.*

(1) *Standardizing the sodium thiosulphate solution.*—Place 20 cc of the potassium bichromate solution, to which has been added 10 cc of the solution of potassium iodid, in a glass-stoppered flask. Add to this 5 cc of strong hydrochloric acid. Allow the solution of sodium thiosulphate to flow slowly into the flask until the yellow color of the liquid has almost disappeared. Add a few drops of the starch paste, and with constant shaking continue to add the sodium thiosulphate solution until the blue color just disappears.

(2) *Weighing the sample.*—Weigh about one-half gram of fat or 0.250 gram of oil [a] on a small watch crystal or by other suitable means. The fat is first melted, mixed thoroughly, poured onto the crystal, and allowed to cool. Introduce the watch crystal into a wide-mouth 16-ounce bottle with ground-glass stopper.

[a] With drying oils which have a very high absorbent power, 0.100 to 0.200 gram should be taken.

(3) *Absorption of iodin.*—The fat or oil in the bottle is dissolved in 10 cc of chloroform. After complete solution has taken place, 25 cc of the iodin solution are added. Allow to stand, with occasional shaking, for 30 minutes. The excess of iodin should be at least 60 per cent of the amount added.

(4) *Titration of the unabsorbed iodin.*—Add 10 cc of the potassium iodid solution and shake thoroughly, then add 100 cc of distilled water to the contents of the bottle. Titrate the excess of iodin with the sodium thiosulphate solution, which is added gradually, with constant shaking, until the yellow color of the solution has almost disappeared. Add a few drops of starch paste, and continue the titration until the blue color has entirely disappeared. Toward the end of the reaction stopper the bottle and shake violently, so that any iodin remaining in solution in the chloroform may be taken up by the potassium iodid solution.

(5) *Setting the value of iodin solution by thiosulphate solution.*—At the time of adding the iodin solution to the fat, two bottles of the same size as those used for the determination should be employed for conducting the operation described above, but without the presence of any fat. In every other respect the performance of the blank experiments should be just as described. These blank experiments must be made each time the iodin solution is used. Great care must be taken that the temperature of the solution does not change during the time of the operation, as acetic acid has a very high coefficient of expansion, and a slight change of temperature makes an appreciable difference in the strength of the solution. Example blank determinations: (1) Forty cubic centimeters iodin solution required 62.05 cc of sodium thiosulphate solution. (2) Forty cubic centimeters iodin solution required 62.15 cc of sodium thiosulphate solution. Mean, 62.1 cc.

Per cent of iodin absorbed:

Weight of fat taken	grams	1.0479
Quantity of iodin solution used	cubic centimeters	40.0
Thiosulphate equivalent to iodin used	do	62.1
Thiosulphate equivalent to remaining iodin	do	30.2
Thiosulphate equivalent to iodin absorbed	do	31.9
Per cent of iodin absorbed ($31.9 \times 0.012 \times 100 \div 1.0479$)		36.53

The following precautions should be exercised in the use of this solution:

1. Great care must be used to prevent change of temperature of the solution, and where any number of determinations are to be made blanks should be measured out at short intervals. This precaution applies as well to the use of the Hübl solution, as the coefficient of the expansion of alcohol is large.

2. When the potassium iodid is added the solution should be thoroughly mixed before the addition of water.

3. The acetic acid must be full strength and pure in order to obtain a solution which will keep well.

[Note by Editor.—In this connection it is suggested that the Hübl and Hanus methods should be rewritten and combined where possible, as they are identical in many respects, and the inclusion of the full text of both in the methods is unnecessary.]

The method for the titer test was adopted as a provisional method. (See Circular 27, Bureau of Chemistry, for the full text of this method.)

ERRATUM.

On page 24, last column, fifth figure from the end, change "1,4468" to "1,4768."

III. DAIRY PRODUCTS.

Twentieth Convention, 1903, Bul. 81, Cir. 13.

On page 36, under "6. Detection of Formaldehyde," designate the method there given as "(a) Hehner's method," and insert the following as a provisional method:

(b) THE HYDROCHLORIC ACID AND FERRIC CHLORID METHOD.[a]

[a] Ann. Rept. Mass. State Board of Health, 1897, p. 558; Food and Drug Reprint, p. 20.

To 10 cc of milk in a porcelain casserole add an equal volume of concentrated hydrochloric acid containing 1 cc of 10 per cent ferric chlorid solution to each 500 cc

of acid. Heat nearly to the boiling point over the free flame, holding the casserole by the handle and giving it a rotary motion to break up the curd. A violet coloration indicates formaldehyde.

Insert also the phloroglucin method as provisional:

(c) PHLOROGLUCIN METHOD.

To the contents of the dish add 3 cc of a phloroglucin solution made by dissolving 1 gram of phloroglucin and 20 grams of sodium hydroxid in sufficient water to make 100 cc. A bright red coloration (not purple) indicates the presence of methyl alcohol in the original sample. When too little hydrogen peroxid is added an orange-yellow color will slowly appear. The hydrogen peroxid, if not fully destroyed, will give rise to a purple color of gradual formation. The cherry or raspberry red produced as a result of methyl alcohol appears quickly after the addition of the reagent, and fades quickly unless quite intense. The intensity of the red color is in proportion to the quantity of methyl alcohol present. If the wood alcohol be as much as 1 part to 20 of ethyl alcohol, its presence will be revealed by this test.

On page 36, after "7. Detection of Borax and Boric Acid," insert the following:

8. DETECTION OF BENZOIC ACID.[a]

Add 5 cc of dilute hydrochloric acid to 50 cc of the milk in a flask and shake to curdle. Then add 150 cc of ether, cork the flask, and shake well. Break up the emulsion which forms by aid of a centrifuge, or if the latter is not available extract the curdled milk by gently shaking with successive portions of ether, avoiding the formation of an emulsion.[b] Transfer the ether extract (evaporated to small volume if large in bulk) to a separatory funnel and separate the benzoic acid from the fat by shaking out with dilute ammonia, which takes out the former as ammonium benzoate. Evaporate the ammonia solution in a dish over the water bath till all free ammonia has disappeared, but before getting to dryness add a few drops of ferric chlorid reagent. The characteristic flesh-colored precipitate indicates benzoic acid. Care should be taken not to add the ferric chlorid till all the ammonia has been driven off, otherwise a precipitate of ferric hydrate is formed.

[a] Leach, Ann. Rept. Mass. State Board of Health, 1902; Food and Drug Reprint, p. 23.

[b] A volume of ether largely in excess over that of the curdled milk has been found to be less apt to form an obstinate emulsion.

9. DETECTION ON SALICYLIC ACID.

Proceed exactly as directed for benzoic acid. On applying the ferric chlorid to the solution after evaporation of the ammonia, the well-known violet color indicates salicylic acid, when present.[c]

[c] These methods for salicylic and benzoic acids while especially applied to milk, from which the ether extracts both fat and preservative, are useful also with modifications for many other food products. The extraction of the ether solution with dilute ammonia, whereby the preservative is removed, permits the subsequent recovery of the ether by distillation.

On page 36, "8. Detection of Foreign Colors" should be renumbered as "10."

On page 39, change heading "8" to "Detection of Foreign Colors," inserting "(a) Cornwall's method[c]" before the method there given. After this method insert the following:

(b) METHOD OF THE MASSACHUSETTS BOARD OF HEALTH FOR ANNATO.

Treat 2 or 3 grams of the melted and filtered fat (freed from salt and water) with warm, dilute sodium hydroxid, and after stirring pour the mixture while warm upon a wet filter, using to advantage a hot funnel. If annato is present, the filter will absorb the color so that when the fat is washed off by a gentle stream of water the paper will be dyed straw color. It is well to pass the warm alkaline filtrate two or three times through the fat on the filter to insure removal of the color. If, after drying the filter, the color turns pink on application of a drop of stannous chlorid solution the presence of annato is assured.

(c) GEISLER'S METHOD FOR AZO COLORS. [d]

A few drops of the clarified fat are spread out on a porcelain surface and a pinch of fuller's earth added. In the presence of various azo dyes a pink to violet-red coloration will be produced in a few minutes. Some varieties of the fuller's earth react much more readily than others with azo colors.

[d] J. Am. Chem. Soc., 1898, **20**: 110.

(d) LOW'S METHOD FOR AZO COLORS. [e]

A small amount of the material to be tested is melted in a test tube, an equal volume of a mixture of one part of concentrated sulphuric acid and four parts of glacial acetic acid is added and the tube is heated nearly to the boiling point, the contents being thoroughly mixed by shaking. The tube is then set aside and after the acid solution has settled out it will be found to be colored wine-red in the presence of azo color, while with pure butter fat comparatively no color will be produced.

[e] J. Am. Chem. Soc., **20**: 889.

(e) DOOLITTLE'S METHOD FOR AZO DYES AND ANNATO. [f]

The melted sample is first filtered. Two test tubes are taken and into each are poured about 2 grams of the filtered fat, which are dissolved in ether. Into one test tube 1 or 2 cc of dilute hydrochloric acid are poured and into the other about the same volume of dilute potassium hydroxid solution. Both tubes are well shaken and allowed to stand. In the presence of azo dye the test tube to which the acid has been added will show a pink to wine-red coloration while the potash solution in the other tube will show no color. If annato has been used, on the other hand, the potash solution will be colored yellow, while no color will be apparent in the acid solution.

[f] Qualitative tests of the curd should be made; see J. Am. Chem. Soc., 1902, **22**: 150.

Also on page 39 strike out section "9. Detection of Anilin Colors," and insert the following:

9. DETECTION OF BORIC ACID IN BUTTER.

Melt about 25 grams of the sample on the water-bath, pour off the fat from the aqueous solution that settles to the bottom of the container, acidify the aqueous solution slightly with hydrochloric acid, and test in the usual manner with turmeric paper for boric acid.

On page 40, under "5. Determination of Fat," insert the heading "(a) Official method[e]" for the method there given, and on page 41, at the close of this method, insert the following as a provisional method:

(b) LYTHGOE'S MODIFICATION OF THE BABCOCK METHOD. [c]

[c] Farrington and Woll, Testing Milk and Its Products, 1st ed., p. 78.

Weigh accurately about 6 grams of the sample in a tared beaker. Add 10 cc of boiling water and stir with a rod till the cheese softens and an even emulsion is

formed, preferably adding a few drops of strong ammonia to aid in the softening and emulsionizing, and keep the beaker in hot water till the emulsion is tolerably complete and free from lumps.

If the sample is a full-cream cheese a Babcock cream bottle is employed. The contents of the beaker, after cooling, are transferred to the test bottle as follows: Add to the beaker about half of the 17.6 cc of sulphuric acid regularly used for the test, stir with a rod and pour carefully into the bottle, using the remainder of the acid in two portions for washing out the beaker. Finally proceed as in the Babcock test for milk. Multiply the fat reading by 18 and divide by the weight of the sample taken to obtain the per cent of fat.

On page 41, at the end of the methods for dairy products, insert the following as a provisional method:

(D) Condensed Milk.

Preparation of the sample.—Mix thoroughly by transferring the contents of the can to a large evaporating dish and working it with a pestle until homogeneous. Weigh 40 grams of the mixed sample in a 100 cc flask, or transfer thereto by washing, and make up to the mark with water.

Total solids.—Dilute a measured portion of the above 40 per cent solution with an equal amount of water, and transfer by a pipette 5 cc of the diluted mixture,' corresponding to 1 gram of the condensed milk, into a tared platinum dish, which is allowed to remain in contact with the live steam of a water bath for at least two hours after the last traces of water have been evaporated to leave an apparently dry residue. Transfer to a desiccator, cool, and weigh.

Ash.—Carefully ignite the residue from the total solids, cool, and weigh.

Fat.[a]—Measure 15 cc of the above 40 per cent solution, corresponding to 6 grams of the condensed milk, into a Babcock test bottle. Fill nearly to the neck with water and add 4 cc of Fehling's copper solution, shake thoroughly and rapidly, separating the precipitated proteids and fat by means of a centrifuge,[b] or the precipitate may be allowed to settle of itself, which it does more quickly in the cold. Withdraw the supernatant sugar-containing liquid by means of a small stemmed pipette with a wisp of wet absorbent cotton twisted over the bottom to serve as a filter. Wipe off the cotton into the bottle on withdrawing the pipette. Give the precipitated proteids and fat two additional washings as above by shaking with water, separating the precipitate, and removing the washings with the pipette. If the precipitate is caked hard after centrifuging, use a stiff platinum wire as a stirrer. Finally add water to an approximate volume of 17.5 cc and 17.5 cc of sulphuric acid, and continue the test as in the Babcock process of milk testing, multiplying the reading by 3 for the percentage of fat in the sample.

[a] Leach, J. Am. Chem. Soc., 1900, **22**: 589.

[b] While the steam-driven centrifuge may be used for this, it is better to centrifuge in the cold, since the heat of the steam-driven machine cakes the precipitate so that it is harder to wash.

Proteids.—Dilute 5 cc of the 40 per cent solution, corresponding to 2 grams of the sample, to about 40 cc and add 0.6 cc of Fehling's copper solution. Nearly neutralize with sodium hydroxid, stopping just short of alkalinity. Pass through a weighed filter paper, wash, dry at 100° C., and weigh. Burn the precipitate in a porcelain crucible, the difference between the weight of the dry precipitate and the weight of the ash being the weight of the proteids and fat. Expressing this in percentage and deducting the per cent of fat previously obtained, the result is the per cent of proteids.

Milk sugar.—Make up the filtrate and washings from the previous operation to 100 cc and determine the lactose either gravimetrically or volumetrically in this solution.

If the volumetric method is used and the solution is of the exact strength directed above, milk sugar may be calculated as follows:

$$\frac{100 \times 0.067}{S \times 0.02} = L$$

wherein L is the per cent of lactose, and S the number of cubic centimeters of milk solution prepared as above necessary to reduce 10 cc of Fehling's solution.

Cane sugar.—Determine by difference, deducting the milk solids (milk sugar + proteids + fat + ash) from the total solids.

[Note by Editor.—No volumetric method having been adopted by the association, it is suggested that the official method for the determination of lactose (Bul. 46, p. 41) be employed.]

Twenty-second Convention, 1905, Bul. 99, Cir. 26.

The following method for the determination of added water in milk was adopted as provisional:

DETECTION OF ADDED WATER.[a]

To 100 cc of milk at a temperature of about 20° C. add 2 cc of 25 per cent acetic acid (sp. gr. 1.0350) in a beaker, and heat the beaker, covered with a watch glass, in a water bath for 20 minutes at a temperature of 70° C. Then place the beaker in ice water for 10 minutes and separate the curd from the serum by filtration through a 12.5 cm plaited filter.

Transfer about 35 cc of the serum to one of the beakers that accompany the control-temperature bath used in connection with the Zeiss immersion refractometer, the bath being of the type with openings in the top for 10 beakers. Place the beaker in one of the openings, use the ground-glass strip at the bottom of the bath, and by means of the regular refractometer heater or similar device maintain a constant temperature of exactly 20° C. in the water surrounding the beaker, using a delicate thermometer, reading to tenths of a degree. Immerse the end of the refractometer in the serum in the beaker, and when the temperature is exactly 20° C. take the reading on the scale.

If the temperature varies from 20° C., the reading may be calculated on that basis by means of a correction table. A reading below 39 indicates added water; between 39 and 40 the sample is suspicious.

[a] Villiers and Bertault, Bul. soc. chim. Par., 1898, **19**: 395; Matthes and Müller, Zts. öffentl. Chem., 1903, **20**: 173; Leach and Lythgoe, J. Am. Chem. Soc., 1904, **26**: 1195.

ERRATUM.

On page 146, "Table X. Per cent of fat and solids not fat in milk," make the following transposition:

Columns 30, 31, 32, sections beginning 8.36, 8.61, 8.10, to the bottom of the page, transfer column 32 to column 30, column 30 to 31, and 31 to 32.

IV. CEREAL PRODUCTS.

In 1902 the associate referee, Mr. A. M. McGill, offered methods for the examination of cereal products for study, which were printed as an unnumbered circular of the Bureau of Chemistry and distributed for criticism. No further action has been taken.

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V. INFANT AND INVALID FOODS.

No methods have been proposed under this section.

VI. SACCHARINE PRODUCTS.

[Note by the Editor.—On page 48, under "11. Determination of Cane Sugar," Clerget's formula there given should be changed to conform with the change made by the association under fruit products (see page 16 of this circular), i. e., $S=\frac{100\,(P-I)}{142.66-\frac{t}{2}}$]

Twentieth Convention, 1903, Bul. 81, Cir. 13.

On page 48, under "12. Determination of Commercial Glucose in Molasses, Sirups, and Honey," make the following changes:

At the end of the second paragraph insert the sentence: "Express results in terms of commercial glucose polarizing at 175°."

Cancel the third paragraph and substitute the following:

In honey, which is composed largely of invert sugar, much more accurate results are attained by polarizing at a temperature of 87° in a water-jacketed tube an inverted, half-normal solution of the sample prepared as follows: Weigh out one-half the normal weight of the sample (13 grams) in a 100 cc graduated flask, dissolve in about 70 cc of water, and add 7 cc of concentrated hydrochloric acid; then heat to 68° C. and cool in the usual manner. After inversion, add a few drops of phenolphthalein and enough sodium hydroxid to neutralize. Discharge the pink color with a few drops of dilute hydrochloric acid, cool again, add from 5 to 10 cc of alumina cream, and make up to the mark. Multiply by 2 the reading at 87° in the 200 mg tube; divide the result by the factor 163 to express the glucose in terms of glucose polarizing at 175°.

Strike out foot note "b," fourth paragraph.

Twenty-second Convention, 1905, Bul. 99, Cir. 26.

The methods for the examination of maple products proposed by Hortvet were adopted as provisional. (See Circular 23, Bureau of Chemistry, for the full text of these methods.)

ERRATUM.

On page 48, under heading "12," fifth and six lines, for "50° C" and "65° C," read "50° V." and "65° V."

VII. CANNED VEGETABLES.

No changes authorized.

VIII. COCOA AND ITS PREPARATIONS.

In 1903 Mr. E. N. Eaton, associate referee, recommended for adoption certain methods (Winton, Silverman, and Bailey, Rept. Conn. Agr. Exper. Stat., 1902, pt. 3, p. 248) for the examination of cocoa

and cocoa products, which were printed as an unnumbered circular of the Bureau of Chemistry and circulated for criticism. No further action has been taken.

IX. TEA AND COFFEE.

Twenty-first Convention, 1904, Bul. 90, Cir. 20.

The methods outlined by the associate referee, Mr. H. C. Lythgoe, were adopted as provisional. (See Bul. 90, p. 38, or Cir. 20, p. 7, for the full text of these methods.)

ERRATA.

Under "13. Alkalinity of the Ash," the editor wishes to call attention to the fact that for all other subjects the methods of the association direct that methyl orange shall be used as indicator in the determination of the alkalinity of the ash.

Under "20. Cane Sugar," second line, for "13.024" read "13."

X. SPICES.

Twentieth Convention, 1903, Bul. 81, Cir. 13.

On page 58, under "13. Determination of Starch by Diastase Method," fifteenth line, strike out the words "copper reduced by," and insert therefor "dextrin resulting from the inversion of."

Twenty-second Convention, 1905, Bul. 99, Cir. 26.

Methods for the analysis of prepared mustard, proposed by the associate referee, A. L. Winton, were adopted as provisional. (For full text of these methods see Cir. 26, p. 9, or Bul. 99.)

XI. VINEGAR.

Twentieth Convention, 1903, Bul. 81, Cir. 13.

On page 65, following section "13," insert Crampton and Simons's method for the detection of caramel as a provisional method:

DETECTION OF CARAMEL (CRAMPTON AND SIMONS[a]).

Add 25 grams of fuller's earth to 50 cc of the vinegar under examination, beat the mixture up in a beaker and let it stand covered half an hour at room temperature, then filter. The determination of the figure representing the color is made with the tintometer upon the liquid before and after treatment, and the difference between the two results gives the percentage of color absorbed.

[a] J. Amer. Chem. Soc., 1899, **21**: 855.

Twenty-second Convention, 1905, Bul. 99, Cir. 26.

Page 68, sixth paragraph, on malic acid, eliminate the following words:

The presence of malic acid distinguishes cider vinegars, though the quantity is often small. * * * If a precipitate be obtained, parallel tests with silver nitrate and

barium chlorid to determine the absence of chlorids and sulphates should be made before the presence of malic acid be considered proved.

XII. FLAVORING EXTRACTS.

Twenty-second Convention, 1905, Bul. 99, Cir. 26.

On page 69 substitute Winton and Bailey's modification of the Hess and Prescott method for the determination of vanillin, coumarin, and acetamid for the present gravimetric methods, i. e., "4. Detection and Determination of Coumarin and Vanillin."

4. Detection and Estimation of Vanillin, Coumarin, and Acetanilid.

(a) determination of vanillin, coumarin, and acetanilid (winton and bailey's modification of the hess and prescott method [a]).

[a] J. Amer. Chem. Soc., 1899, **21**: 256; 1902, **24**: 1128; 1905, **27**: 719.

Weigh out 25 grams into a 200 cc beaker with marks showing volumes of 25 and 50 cc. Dilute to the 50 cc mark, and evaporate in a water bath to 25 cc at a temperature in the bath of not more than 70° C. Dilute a second time to 50 cc, and evaporate to 25 cc. Add normal lead acetate solution drop by drop until no more precipitate forms. Stir with a glass rod to facilitate flocculation of the precipitate, filter through a moistened filter and wash three times with hot water, taking care that the total filtrate does not measure more than 50 cc. Cool the filtrate and shake with 20 cc of ether in a separatory funnel. Remove the ether to another separatory funnel and repeat the shaking of the aqueous liquid with ether three times, using 15 cc each time. Shake the combined ether solutions four or five times with 2 per cent ammonia, using 10 cc for the first shaking and 5 cc for each subsequent shaking. Set aside the combined ammoniacal solutions for the determination of vanillin.

Wash the ether solution into a weighed dish and allow the ether to evaporate at the room temperature. Dry in a desiccator, and weigh. Stir the residue for fifteen minutes with 15 cc of petroleum ether (boiling point 30° to 40° C.), and decant the clear liquid into a beaker. Repeat the extraction with petroleum ether two or three times. Allow the residue to stand in the air until apparently dry, completing the drying in a desiccator. Weigh, and deduct the weight from the weight of the residue obtained after the ether evaporation, thus obtaining the weight of the coumarin. This residue, if acetanilid, should have a melting point of about 112° C., and respond to Ritsert's qualitative tests.

Allow the petroleum ether extract to evaporate at room temperature. If it is pure coumarin, it should have a melting point within a few degrees of 67° C., and respond to Leach's test.

Slightly acidulate the ammoniacal solution, reserved for vanillin, with 10 per cent hydrochloric acid. Cool, and shake out in a separatory funnel with four portions of ether, as described for the first ether extraction. Evaporate the ether at room temperature in a weighed platinum dish, dry over sulphuric acid, and weigh.

If acetanilid has not been previously detected, this residue should be pure vanillin, with a melting point within a few degrees of 80° C.

If acetanilid has been detected, dissolve the residue in 15 cc of 10 per cent ammonia, and shake out twice with an equal volume of ether. Evaporate the ether solution at room temperature, dry in a desiccator, and weigh. Deduct this weight from the previous weight, thus obtaining the weight of pure vanillin. The total weight of the acetanilid is obtained by adding the weight of this last extract to that of the residue previously obtained, and identified as acetanilid.

In doubtful cases the ammoniacal solution should be acidified, shaken out with ether, and the melting point of the vanillin, obtained by evaporation at room temperature, determined.

Following the above, under section "4," insert Leach's test for coumarin as a provisional method:

(b) DETECTION OF COUMARIN (LEACH'S METHOD[a]).

Applied to dry crystals or to the residue from the ether extract of the dealcoholized ammoniacal sample of vanilla extract, in the gravimetric determination of coumarin, to confirm its identity. Dissolve a few of the crystals or the small crystalline residue in a few drops of hot water, filter if necessary, and add to the clear solution a little iodin in potassium iodid reagent.[b] In presence of coumarin a brown precipitate will form, which on stirring or shaking will soon gather in dark-green flecks, leaving a clear, brown solution. The reaction is especially marked if the iodin reagent is applied with a glass rod to the few drops of solution to be tested on a white plate or tile.

[a] Leach, Food Inspection and Analysis, p. 738.

[b] Dissolve 2 grams of potassium iodid in 100 cc of water and saturate solution with iodin.

Under heading "4," and following section "(b)," insert the colorimetric ferrous-sulphate method for the determination of vanillin as a provisional method:

(c) DETERMINATION OF VANILLIN (COLORIMETRIC METHOD[a]).

Measure 2 cc of the vanilla extract into a test tube and add about 5 cc of lead hydrate reagent.[b] Mix thoroughly and pour upon a small wet filter and collect filtrate and washings in a 50 cc graduated Nessler tube. Add an excess of bromin water (three or four drops), and sufficient freshly prepared 10 per cent ferrous sulphate solution to produce the maximum bluish-green color that will result if vanillin is present, and fill to the mark with water.

Prepare a standard solution of vanillin by dissolving 50 mg of pure vanillin in 25 cc of alcohol and make up to 100 cc with water. Make up a series of color standards, taking for instance, 0.5, 1, 1.5, 2, 2.5, 3, . . . cc of the standard vanillin solution in 50 cc Nessler tubes, each being treated with two or three drops of bromine water and with an excess of ferrous-sulphate solution, and made up to the 50 cc mark. Match the color from the sample extract with the appropriate one of the color series and thus calculate the amount of vanillin present.

If, for example, 2 cc of a sample extract, treated as above, are found to give a color corresponding in depth to that produced by 5.5 cc of the standard solution, the amount of vanillin would be thus calculated:

100 cc of standard vanillin solution contain 0.05 gram vanillin.

1 cc of standard vanillin solution contains 0.0005 gram vanillin.

5.5 cc of standard vanillin solution contain 0.00275 gram vanillin.

Since 2 cc of the sample are equivalent to 5.5 cc of the standard solution, it follows that 2 cc of the sample contain 0.00275 gram of vanillin; therefore 100 cc of the sample contain 0.1375 gram of vanillin.

[a] Leach, Food Inspection and Analysis, p. 735.

[b] Dissolve 200 grams of lead acetate in 850 cc of water, filter, and add an excess of potassium or sodium hydroxid. Let the precipitate settle and wash thoroughly by decantation with repeated portions of water till perfectly neutral. Keep in 500 cc of water in the reagent bottle, and shake to form an emulsion-like mixture before adding to decolorize.

Under heading "4," and following section "(c)," insert the following method as provisional:

[Note by the Editor.—This method was not acted upon directly by the association, but its adoption is implied in section "4, (a)," in which its use is required.]

(d) RITSERT'S TESTS FOR ACETANILID.[a]

Boil the acetanilid, obtained as described under (a), in a small beaker for two or three minutes with 2 to 3 cc of concentrated hydrochloric acid, cool, divide into three portions, and test in small tubes (4–5 mm inside diameter) as follows:

(1) *Indophenol reaction.*—To one portion add carefully 1 to 3 drops of a solution of chlorinated lime (1:200) in such a manner that the two solutions do not mix. A beautiful blue color formed at the juncture of the two liquids indicates acetanilid.

(2) To another portion add a small drop of potassium permanganate solution. A clear, green color is formed if any appreciable amount of acetanilid is present.

(3) Mix the third portion with a small drop of 3 per cent chromic-acid solution. Acetanilid gives a yellow-green solution, changing to dark green on standing five minutes, and forming a dark blue precipitate on addition of a drop of caustic-potash solution.

[a] Pharm. Ztg., 1888, **33**: 383; Abs. Zts. anal. Chem., 1888, **27**: 667.

Leach and Lythgoe's refractometric method for the detection of methyl alcohol was adopted as a provisional method in the analysis of extracts.

DETECTION AND DETERMINATION OF METHYL ALCOHOL IN VANILLA EXTRACT (METHOD OF LEACH AND LYTHGOE[a]).

Submit the alcoholic distillate obtained in the determination of alcohol to refraction with the immersion refractometer at exactly 20° C. and note the reading. If on reference to the table the refraction shows the percentage of alcohol agreeing with that obtained from the specific gravity in the regular manner, it may safely be assumed that no methyl alcohol is present. If, however, there is an appreciable amount of methyl alcohol the low refractometer reading will at once indicate the fact. If the absence in the solution of other refractive substances than water and the alcohols is assured this qualitative test by difference in refraction is conclusive.

Addition of methyl to ethyl alcohol decreases the refraction in direct proportion to the amount present; hence the quantitative calculation is readily made by interpolation in the table, using the figures for pure ethyl and methyl alcohol of the same alcoholic strength as the sample.

Example: Suppose the distillate from a vanilla extract made up to the original volume of the measured portion taken for the alcohol determination has a specific gravity of 0.97350, corresponding to 18.38 per cent alcohol by weight, and has a refraction of 35.8 on the immersion refractometer at 20°. By interpolation in the refractometer table the readings of ethyl and methyl alcohol corresponding to 18.38 per cent alcohol are 47.2 and 25.4, respectively, the difference being 21.8; 47.2—35.8= 11.4; (11.4÷21.8) 100=52.3, showing that 52.3 of the alcohol present is methyl.

[a] J. Amer. Chem. Soc., 1905, **27**: 964.

Scale readings on Zeiss immersion refractometer at 20° C., corresponding to each per cent by weight of ethyl and methyl alcohols.

Per cent alcohol by weight.	Scale readings.		Per cent alcohol by weight.	Scale readings.		Per cent alcohol by weight.	Scale readings.		Per cent alcohol by weight.	Scale readings.	
	Methyl alcohol.	Ethyl alcohol.		Methyl alcohol.	Ethyl alcohol.		Methyl alcohol.	Ethyl alcohol.		Methyl alcohol.	Ethyl alcohol.
0	14.5	14.5	26	30.3	61.9	51	39.7	91.1	76	29.0	101.0
1	14.8	16.0	27	30.9	63.7	52	39.6	91.8	77	28.3	100.9
2	15.4	17.6	28	31.6	65.5	53	39.6	92.4	78	27.6	100.9
3	16.0	19.1	29	32.2	67.2	54	39.5	93.0	79	26.8	100.8
4	16.6	20.7	30	32.8	69.0	55	39.4	93.6	80	26.0	100.7
5	17.2	22.3	31	33.5	70.4	56	39.2	94.1	81	25.1	100.6
6	17.8	24.1	32	34.1	71.7	57	39.0	94.7	82	24.3	100.5
7	18.4	25.9	33	34.7	73.1	58	38.6	95.2	83	23.6	100.4
8	19.0	27.8	34	35.2	74.4	59	38.3	95.7	84	22.8	100.3
9	19.6	29.6	35	35.8	75.8	60	37.9	96.2	85	21.8	100.1
10	20.2	31.4	36	36.3	76.9	61	37.5	96.7	86	20.8	99.8
11	20.8	33.2	37	36.8	78.0	62	37.0	97.1	87	19.7	99.5
12	21.4	35.0	38	37.3	79.1	63	36.5	97.5	88	18.6	99.2
13	22.0	36.9	39	37.7	80.2	64	36.0	98.0	89	17.3	98.9
14	22.6	38.7	40	38.1	81.3	65	35.5	98.3	90	16.1	98.6
15	23.2	40.5	41	38.4	82.3	66	35.0	98.7	91	14.9	98.3
16	23.9	42.5	42	38.8	83.3	67	34.5	99.1	92	13.7	97.8
17	24.5	44.5	43	39.2	84.2	68	34.0	99.4	93	12.4	97.2
18	25.2	46.5	44	39.3	85.2	69	33.5	99.7	94	11.0	96.4
19	25.8	48.5	45	39.4	86.2	70	33.0	100.0	95	9.6	95.7
20	26.5	50.5	46	39.5	87.0	71	32.3	100.2	96	8.2	94.9
21	27.1	52.4	47	39.6	87.8	72	31.7	100.4	97	6.7	94.0
22	27.8	54.3	48	39.7	88.7	73	31.1	100.6	98	5.1	93.0
23	28.4	56.3	49	39.8	89.5	74	30.4	100.8	99	3.5	92.0
24	29.1	58.2	50	39.8	90.3	75	29.7	101.0	100	2.0	91.0
25	29.7	60.1									

XIII. FRUITS AND FRUIT PRODUCTS.

[Note by the Editor.—Since the publication of Bul. 65, in 1902, several changes have been made not only in the methods under fruit products but also in the sugar methods which make it difficult to arrange the fruit product methods, the incorporation of only such changes as have been directly authorized under this head leaving the context incomplete or illogical in some cases. In the following statement of the changes and additions, therefore, the changes made which are unauthorized by specific action but are believed to be the will of the association are printed in italics.]

Twentieth Convention, 1903, Bul. 81, Cir. 13.

On page 78, under "12. Polarization," substitute the method for the determination of sucrose in the absence of raffinose (Proceedings Nineteenth Convention, 1902, Bul. 73, p. 57; Proceedings Twentieth Convention, 1903, Bul. 81, p. 230).

12. Polarization.

Dissolve half the normal weight of jelly or other fruit product, or the normal weight of juices or fresh fruits, in a sufficient quantity of water in a 100 cc flask, add an excess of lead subacetate (from 5 to 10 cc, see footnote Bul. 65, p. 84), filter, and polarize in a 200-mm tube at 20° C. Regard the polariscope reading as the direct reading, or polarization before inversion.

Take 50 cc of the clarified solution freed from lead, add 25 cc of water, and add, little by little, while rotating the flask, 5 cc of hydrochloric acid containing 38.8 per cent of the acid; and heat the contents of the flask, after mixing, on a water bath heated to 70° C. The temperature of the solution in the flask should reach 67° to 70° in two and one-half to three minutes. Maintain a temperature of as nearly 69° as possible during seven to seven and one-half minutes, making a total time of heating of ten minutes. Remove the flask and cool the contents rapidly to 20° C., and dilute the solution to 100 cc. Polarize this solution in a tube provided with a lateral branch and a water jacket, passing a current of water around the tube to maintain a temperature of 20° C. Multiply the invert reading, made at 20° C., by 2.

Or—

Take 50 cc of the clarified solution freed from lead, add 5 cc of hydrochloric acid containing 38.8 per cent of acid, set aside during a period of twenty-four hours at a temperature not below 20° C.; or if the temperature be above 25° C. set aside for ten hours. Make up to 100 cc at 20° C. and polarize.

13. Determination of Sucrose.

(a) by polarization.

Calculate *sucrose* from the direct and the invert *polariscopic* readings according to *the following formula:*

When the polarizations are made at 20° C.:

$$S=\frac{100\,(P-I)}{142.66-\frac{20°}{2}}=0.7538X\,(P-I)$$

P=the direct reading.
I=the invert reading.
S=the percentage of sucrose.

Should the temperature (t) vary from 20°, which is permissible within narrow limits, in the absence of raffinose use the following formula:

$$S=\frac{100\,(P-I)}{142.66-\frac{t}{2}}$$

On page 78, section 13, b, line 8, change "1 per cent" to "0.50 per cent."

(b) by reduction.

Where only a small amount of cane sugar is present it is best determined by calculation from the increase in reducing sugars after inversion. For this purpose treat 5 grams of jelly, sirup, or other fruit product *dissolved in a sufficient amount of water,* or 25 grams of juice or fresh fruit, with lead subacetate in excess, *make up to 100 cc and filter. Remove the excess of lead with sodium sulphate and invert 50 cc in a 100 cc flask with 5 cc of hydrochloric acid. After inversion neutralize the acid with sodium hydroxid and increase the volume to 100 cc.* Dilute so that the solution does not contain more than 0.50 per cent of reducing sugar. *The clarified products obtained for polarization under "13" before and after inversion may also be used after suitable dilution for the determination of the reducing power.* The per cent increase in reducing sugar after inversion multiplied by 0.95 equals per cent of cane sugar.

On page 78, section 14, lines 8 and 9, for the words "Use Allihn's method for the determination (p. 49)," substitute "Use the official method for the determination of invert sugar as given in Bul. 46, p. 33 (c) (1) (a) and (b)."

On page 78, strike out section "15. Determination of Dextrin" and substitute therefor "Determination of Glucose," referring to method given on page 48, section 12.

15. Determination of Glucose.

Dissolve half the normal weight of jelly or other fruit product, or the normal weight of juices, clarify, and invert as directed under polarization (p. 16). Polarize in jacketed tube at 86° C., and calculate the percentage of commercial glucose as directed on page 48, Bulletin 65.

XIV. FERMENTED AND DISTILLED LIQUORS.

Twentieth Convention, 1903, Bul. 81, Cir. 13.

On page 96, under "2. Determination of Alcohol," for the words "Measure 50 cc of the sample (at 15.6° C.) into a distilling flask" substitute the following: "Weigh or measure (at 15.6° C.) in a distilling flask 20 to 25 cc of the sample."

Under "3. Determination of Extract," substitute the following method for the one there given:

Weigh or measure (at 15.6° C.) 100 cc of the sample, evaporate nearly to dryness on the water bath, then transfer to a water oven, and dry at the temperature of boiling water.

Under "5. Determination of Acidity," substitute the following method for the one there given:

Titrate 100 cc (or 50 cc diluted to 100 cc if the sample is dark in color) with decinormal barium hydroxid, using phenolphthalein as indicator. The number of cubic centimeters employed is multiplied by 0.006 for the acidity expressed in grams of acetic acid per 100 cc.

Under "7. Determination of Fusel Oil," strike out the third paragraph and substitute the following:

Add a small quantity of alkali to 200 cc of the sample under consideration and distill slowly till about 175 cc have passed over, allow the distilling flask to cool, add 25 cc of water, and distill again until the total distillate measures 200 cc. Dilute the distillate to exactly 30 per cent by volume[b] (sp. gr. 0.96541 at 15.6°).

On page 98, strike out the method given under "9. Determination of Ethereal Salts" and substitute the following:

9. Determination of Ethereal Salts.

Neutralize the residue left after distillation in the fusel oil determination with N/10 H_2SO_4 and add an excess of 10 cc of the acid. Let stand five minutes and make up to 200 cc. Titrate 2 portions of 25 cc each, using as indicators methyl orange in the first and phenolphthalein in the second. The difference gives the amount of alkali necessary to neutralize the organic acids in 25 cc of the sample. By subtracting from this figure the number of cubic centimeters of alkali required for the free acids, and multiplying the result by 0.0088, the number of grams of ethereal salts (calculated as ethyl acetate) in 25 cc of the sample is determined.

[Note by the Editor.—See also action taken in 1905 in regard to this section.]

Twenty-first Convention, 1904, Bul. 90, Cir. 20.

The Amthor test for caramel as modified for distilled liquors by Lasché was adopted as provisional.

DETECTION OF CARAMEL (AMTHOR METHOD MODIFIED BY LASCHÉ).

Add 10 cc of paraldehyde to 5 cc of the sample contained in a test tube and shake. Then add absolute alcohol, a few drops at a time, shaking after each addition until the mixture becomes clear. Allow to stand. Turbidity (after ten minutes) is indication of caramel.—The Brewer Distiller, May, 1903.

Twenty-second Convention, 1905, Bul. 99, Cir. 26.

On page 97, substitute the following method for the determination of aldehydes for the method given under heading "8":

Determine the aldehydes in the distillate prepared for the esters. Five to 10 cc of the distillate are diluted to 50 cc with aldehyde-free alcohol (50 per cent by volume), 25 cc of the reagent added, and allowed to stand for 20 minutes at 15° C. The solutions and the reagents should be at 15° C. before they are mixed.

Reagent.—Dissolve 0.5 gram of pure fuchsin in 500 cc of water, then add a water solution of sulphur dioxid, equivalent to 5 grams of sulphur dioxid, and make the whole up to 1 liter. This solution can be used as soon as it becomes colorless and will keep for several days.

Aldehyde-free alcohol is prepared by treating ordinary 95 per cent alcohol with potassium hydroxid and distilling. Then this distillate is treated with about 3 grams to the liter of metaphenelenediamin hydrochlorate, and heated with a reflux condenser for several hours, then distilled slowly, not keeping the first 100 cc nor the last 100 cc. This will give an alcohol which will give only the slightest tinge of color when treated with the reagent.

The standard aldehyde solution is treated in the same way as the distillate, and the color of the standard must be very close to the color of the sample.

On page 98 substitute the following method for the one given under "9. Determination of Ethereal Salts" (see change adopted in 1903):

9. DETERMINATION OF ETHEREAL SALTS.

In 50 cc of the distillate neutralize the free acid with decinormal alkali, using phenolphthalein as an indicator, then add 25 cc decinormal alkali and either heat for one hour with a reflux condenser, cool and titrate with decinormal acid, or allow the solution to stand over night in a stoppered flask with the excess of alkali, then heat with a *tube* condenser for one-half hour *below the boiling point*, cool and titrate. The number of cubic centimeters of decinormal alkali used in the saponification of the esters is calculated as ethyl acetate. *One cubic centimeter of decinormal alkali equals 0.0088 gram ethyl acetate.*

The distillate for esters, aldehydes, and furfural is prepared in the following manner: Add 25 cc of water to 200 cc of the whisky and distill until 200 cc are distilled off. It is advisable to use a mercury valve in order to prevent loss of alcohol, and the distillation should be made slowly.

[Note by the Editor.—In this method the words in italics indicate slight changes and an addition made subsequent to the action of the association, by Mr. Tolman, who submitted the method.]

On page 98 strike out the method given under "10. Determination of Furfural," and substitute the following:

From 10 to 20 cc of the distillate are diluted to 50 cc with furfural-free alcohol (50 per cent by volume). To this add 2 cc of colorless anilin and one-half cubic centimeter of hydrochloric acid (sp. gr. 1.125) and keep for 15 minutes in a water bath at about 15° C.

Prepare standards of known strength in the same way.

Add the Trillat test for the detection of methyl alcohol in distilled liquors to the provisional methods.

DETECTION OF METHYL ALCOHOL.[a]

(a) TRILLAT'S METHOD.

To 50 cc of spirit add 50 cc of water and 8 grams of lime, and fractionally distill by the aid of Glinsky bulb-tubes. The first 15 cc of the distillate are then diluted to 150 cc, mixed with 15 grams of potassium bichromate and 70 cc of sulphuric acid (1:5), and left for one hour, being shaken at intervals. This liquid is then distilled, the first 25 cc being rejected and distillation stopped when 100 cc have been collected.

Fifty cubic centimeters of distillate are mixed with 1 cc of rectified dimethyl-anilin, transferred to a stout, tightly stoppered flask, and kept on bath at 70° to 80° C., for three hours, with occasional shaking. The liquid is then rendered distinctly alkaline with sodium hydroxid and the excess of dimethyl-anilin distilled off, distillation being stopped when 25 cc have passed over.

The residue in the flask is acidified with acetic acid and shaken, and a few cubic centimeters tested by adding 4 or 5 drops of water with lead dioxid in suspension (1 gram in 100 cc). If it be present a blue coloration occurs and becomes more developed by boiling.

Note: Ethyl alcohol thus treated yields a blue coloration, changing immediately to green, afterwards to yellow, and becoming colorless when boiled.

[a] A. Trillat, Analyst, 1899, 24: 13, 211–212.

Add the Riche and Bardy test for the detection of methyl alcohol in distilled liquors to the provisional methods.

(b) RICHE AND BARDY'S METHOD.[a]

[a] Allen's Commercial Organic Analysis, 3d ed., vol. 1, p. 80.

The following process has been devised by MM. Riche and Bardy for the detection of methyl alcohol in commercial spirit of wine. It depends on the formation of methyl anilin violet.

Ten cubic centimeters of the sample of alcohol, previously rectified if necessary over potassium carbonate, are placed in a small flask with 15 grams of iodin and 2 grams of red phosphorus. Methyl and ethyl iodids are formed, and should be distilled off into 30 cc of water. The heavy oily liquid which settles to the bottom is separated from the water and transferred to a flask containing 5 cc of anilin. The flask should be placed in cold water, in case the action should be violent; or if necessary the reaction may be stimulated by gently warming the flask. After one hour the product is boiled with water and solution of soda added, when the bases rise to the top as an oily layer, which may be drawn off with a pipette after filling the flask with water up to the neck. One cubic centimeter of the oily liquid thus obtained is next oxidized by adding to it 10 grams of a mixture of 100 parts of clean sand, 2 of common salt, and 3 of cupric nitrate. After being thoroughly mixed, the whole is introduced into a glass tube and heated to 90° C. for eight to ten hours. The prod-

uct is exhausted with warm alcohol, the liquid filtered, and made up with alcohol to 100 cc. If the sample of spirit be pure, the tint of the liquid is red, but in presence of 1 per cent of methyl alcohol it has a distinct violet shade; with 2.5 per cent the shade is very distinct, and still more so with 5 per cent. To detect more minute quantities of methyl alcohol, 5 cc of the colored liquid are diluted to 100 cc with water, and 5 cc of this again diluted to 400 cc. The liquid thus obtained is heated in porcelain, and a fragment of white merino (free from sulphur) immersed in it for half an hour. If the alcohol be pure, the wool will remain white; but if methylated, the fiber will become violet, the depth of tint giving a fair approximate indication of the proportion of methyl alcohol present.

Add the method of Leach and Lythgoe for the estimation of ethyl and methyl alcohol in mixtures of the same, to the provisional methods. This mixture is modified for different liquors, and the following is more specifically for whiskies:

(c) LEACH AND LYTHGOE METHOD.

Weigh 50 grams of sample, mix with 75 cc of water, and distill 100 cc. Determine alcohol in the distillate as directed under "2. Determination of Alcohol," and proceed as directed on page 14.